

# PATENT SPECIFICATION

NO DRAWINGS

Inventor: GRANT CRANE

820.601



Date of Application and filing Complete Specification: Sept. 23, 1957.

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Index at acceptance:—Class 2(6), P2C(6A:8B:8C:19), P2(D1A:K7), P2T(1A:2A).

International Classification:—C08d.

## COMPLETE SPECIFICATION

### Improvements in 'Stabilized' Oil-Extended Synthetic Rubber

We, THE FIRESTONE TIRE & RUBBER COMPANY, a corporation organized under the laws of the United States of America, do hereby certify that the following is a full and complete specification of the invention which we claim as our own, and which is embodied in the accompanying drawings, and which is a response to conventional GR—S stabilizers.

## ERRATA

SPECIFICATION NO. 820,601

Page 3, line 8, for "axide" read "oxide"

Page 4, line 57, for "oil refined" read "oil-extended"

Page 4, line 58, after "polymer" insert "or copolymer"

THE PATENT OFFICE,  
26th April, 1960

DS 74460/1(3)/3951 200 4/60 DL

25 produced at a saving over the straight synthetic rubber. Since the oil employed for extension of the rubber acts as a plasticizer for the rubber, it has been customary to employ stiffer synthetic rubbers for oil-extension than are employed in the absence of oil. For example, commercial GR—S has usually been manufactured with a Mooney plasticity of about 50 to 60 for use without oil extension, whereas 30 the GR—S employed for producing oil-extended polymers usually has an initial Mooney plasticity of at least 85 or 90, and generally exceeds 125. Tyre treads produced from the 35 oil-extended rubber of such high initial Mooney plasticity have exhibited very good abrasion resistance, the wear ratings being much higher than would be predicted from a consideration of the diluting effect of the 40 oil on the rubber. Thus, the practice of utilizing oil-extended GR—S for tyre treads has become very popular in recent years.

45 Whereas regular GR—S has presented no great stabilization problems in recent years, the oil-extended polymers have not always [Price 3s. 6d.]

of the type just discussed.

It is therefore an object of the invention to provide a simple, economical and effective method of stabilizing synthetic rubber. It is also an object to provide improved oil-extended synthetic rubbers. Furthermore, it is an object of the invention to provide economical, effectively stabilized, oil-extended synthetic rubbers readily acceptable by the tyre industry. 70 75

The objects of the invention are simply and effectively realized by incorporating into oil-extended synthetic rubbers a relatively small amount of a finely-divided, light coloured, semi-reinforcing, inorganic pigment. Suitable 80 pigments include zinc oxide, magnesium oxide, silicon dioxide and calcium silicate. The fine particle size of these pigments is generally guaranteed by the commercial methods of preparing them, usually involving a precipitation, 85 either in the wet way, or in the case of zinc oxide, precipitation from a gas mixture. The pH of zinc oxide, magnesia and calcium silicate pigments is inherently higher than 7.0.

The invention is illustrated by the follow- 90

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## COMPLETE SPECIFICATION

### Improvements in Stabilized Oil-Extended Synthetic Rubber

We, THE FIRESTONE TYRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of 1200 Firestone Parkway, Akron 17, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following:—

This invention relates to oil-extended synthetic rubbery polymers and copolymers of a butadiene-1,3, and it especially relates to an oil-extended rubbery copolymer of butadiene and styrene having improved stability upon storage prior to vulcanization.

Oil-extended synthetic rubbers, especially oil-extended GR—S, have become very popular in recent years for a number of reasons. The oils employed commercially are much cheaper than the synthetic rubber itself, so that the oil-extended synthetic rubber is produced at a saving over the straight synthetic rubber. Since the oil employed for extension of the rubber acts as a plasticizer for the rubber, it has been customary to employ stiffer synthetic rubbers for oil-extension than are employed in the absence of oil. For example, commercial GR—S has usually been manufactured with a Mooney plasticity of about 50 to 60 for use without oil extension, whereas the GR—S employed for producing oil-extended polymers usually has an initial Mooney plasticity of at least 85 or 90, and generally exceeds 125. Tyre treads produced from the oil-extended rubber of such high initial Mooney plasticity have exhibited very good abrasion resistance, the wear ratings being much higher than would be predicted from a consideration of the diluting effect of the oil on the rubber. Thus, the practice of utilizing oil-extended GR—S for tyre treads has become very popular in recent years.

Whereas regular GR—S has presented no great stabilization problems in recent years, the oil-extended polymers have not always

responded to conventional GR—S stabilizers. For example, a certain type of oil-extended GR—S produced at one synthetic rubber plant has exhibited satisfactory stability during storage, whereas the same type of oil-extended rubber produced at another plant has given much trouble, especially after storage in the hot summer months, the Mooney plasticities sometimes dropping from the original 55 to 65 to values of less than 20. Such "soupy" rubber is distinctly undesirable. There has never been a satisfactory explanation of why this oil-extended rubber from one plant has performed well, whereas the same type of rubber from another plant has exhibited poor stability. Perhaps a trace of contaminants has catalyzed the deterioration of the rubber from the one plant. In any event, an urgent need has arisen for a simple and economical method of stabilizing oil-extended synthetic rubbers of the type just discussed.

It is therefore an object of the invention to provide a simple, economical and effective method of stabilizing synthetic rubber. It is also an object to provide improved oil-extended synthetic rubbers. Furthermore, it is an object of the invention to provide economical, effectively stabilized, oil-extended synthetic rubbers readily acceptable by the tyre industry.

The objects of the invention are simply and effectively realized by incorporating into oil-extended synthetic rubbers a relatively small amount of a finely-divided, light coloured, semi-reinforcing, inorganic pigment. Suitable pigments include zinc oxide, magnesium oxide, silicon dioxide and calcium silicate. The fine particle size of these pigments is generally guaranteed by the commercial methods of preparing them, usually involving a precipitation, either in the wet way, or in the case of zinc oxide, precipitation from a gas mixture. The pH of zinc oxide, magnesia and calcium silicate pigments is inherently higher than 7.0.

The invention is illustrated by the follow-

[Price 3s. 6d.]

ing examples (all parts and percentages throughout the present specification are by weight, unless otherwise stated):

#### EXAMPLE 1

5 A rubbery butadiene-styrene copolymer synthetic rubber was produced in accordance with the specification for GR—S 1710 by aqueous emulsion polymerization in an iron pyrophosphate formula at 5° C. The resulting high-  
10 Mooney polymer, in latex form, was conventionally stabilized by addition of 1.25 phr (parts per 100 parts of the rubber) phenyl-beta-naphthylamine, added as a 20% dispersion containing 2% of the dispersing agent, "Daxad" (registered Trade Mark) No. 11  
15 (sodium salt of condensed alkyl, aryl sulphonic acid). The latex was warmed with gentle mechanical stirring on an electrical hot plate at 50° C. to 60° C. A high aromatic oil, 37.5  
20 phr Shell SPX—97 was emulsified to produce a 50% oil dispersion in 2.5% potassium oleate, and the resulting emulsion was separately warmed to 50° C. to 60° C. and then mixed into the warm latex. The resulting convention-  
25 ally stabilized latex was divided into five portions, one portion becoming a control. To each of the other four portions there was added 2.75 phr (2 parts per 100 parts extended polymer) of zinc oxide (A), magnesium  
30 oxide (B), calcium silicate (C) and silicon dioxide having a pH of approximately 8.4 (D),

respectively, and each of the four latex preparations was stirred for about 10 minutes.

The control latex and each of the four test latices was separately coagulated by the "shock" (or "lump") method. The warm oil-extended latex was poured with stirring into 4.8 cc./gram of unextended latex of salt-acid solution (4% sodium chloride plus 0.4% sulphuric acid). The volume of salt-acid coagulant was approximately the same as the volume of the unextended latex. Stirring was continued until coagulation was complete. The coagulum was allowed to remain in the serum for about one minute and then was removed and passed through a laboratory pelletizer within about five minutes. The wet pellets were allowed to stand overnight and then were dried eight hours in a 60° C. forced draught oven. Portions of the dried oil-extended polymers were set aside for determination of the Mooney plasticity. Each polymer was then aged for six hours in a 93.5° C. (200° F.) oven, and a portion of each sample was then taken for Mooney plasticity determination. Ageing in the 200° F. oven was continued until a substantial portion of the surface of each polymer was glazed in appearance, at which time the sample was removed from the oven and the final Mooney plasticity determined. The data thus obtained are set out in Table I.

TABLE I

Stabilization of Oil-Extended GR-S with various pigments.

Sample	Initial Mooney Plasticity (ML4)	ML4 After 6 hrs. @ 200°F.	Final ML4
Control	63.0	40.0	19.0 @ 11.8 hrs.
A (zinc oxide)	67.0	64.5	23.5 @ 24.6 hrs.
B (magnesium oxide)	68.1	49.0	21.5 @ 24.6 hrs.
C (calcium silicate)	65.2	46.0	29.5 @ 11.8 hrs.
D (silicon dioxide)	67.2	62.0	33.0 @ 19.8 hrs.

65 It is readily apparent from Table I that the four basic pigments protected the oil-extended rubber appreciably by slowing down the loss in Mooney plasticity value upon heating, the zinc oxide and silicon dioxide being outstanding in their protective effects.  
70 The heating period of six hours at 200° F. is considered to be equivalent to several months ageing under ordinary storage conditions.

#### EXAMPLE 2

In the manner described in Example 1, additional tests were made on three commercial samples of zinc oxide, employed in different proportions. The details concerning the various samples and testing results obtained are shown in Table II, in which the percentages of zinc oxide are given in phr extended polymers.

TABLE II

Sample	Original ML4	ML4 After 6 hrs. @ 200°F.	ML4 Loss/hr.
Control	61.0	52.0	1.5
2.0% zinc oxide (1)	61.5	57.5	0.7
1.0% zinc oxide (1)	62.5	57.5	0.8
0.5% zinc oxide (1)	61.5	58.0	0.6
2.0% zinc oxide (2)	60.5	57.5	0.5
2.0% zinc oxide (3)	61.0	58.0	0.5

## EXAMPLE 3

- An oil-extended rubbery polymer of the GR—S 1710 type was produced as in Example 1. A portion was taken as the control, a second portion was stabilized by addition of 1.0 phr zinc oxide, and a third portion was stabilized by addition of 2.0 phr zinc oxide. The stabilizing effect of the zinc oxide on this oil-extended rubber is shown in Table IIIA.

TABLE IIIA

Oil-Extended Rubber	Initial ML4	ML4 After 6 hrs. at 200°F.
Control	66.5	13.0
1.0 phr zinc oxide (G)	65.0	62.0
2.0 phr zinc oxide (H)	67.5	60.5

Portions of the three unaged oil-extended samples of Table IIIA were compounded in a tyre tread formula, and the normal physical properties were obtained on the vulcanized rubber compositions. The formulas and test results are shown in Table IIIB.

TABLE IIIB

Parts by weight per 100 of unextended rubber

Ingredients	Control Stock	G Stock	H Stock
Control Rubber	137.5	—	—
G Rubber	—	137.5	—
H Rubber	—	—	137.5
HAF Carbon Black	70	70	70
Zinc Oxide	3.0	2.0	1.0
Stearic Acid	2.0	2.0	2.0
Processing Oil	7.0	7.0	7.0
Sulphur	2.0	2.0	2.0
Accelerator	1.2	1.2	1.2
Cure 90 minutes @ 280°F.			
Tensile Strength (psig)	3050	3250	3100
300% Modulus (psig)	1650	1700	1625
Elongation %	550	500	520

Table IIIA shows the excellent stabilizing effect of zinc oxide on oil-extended synthetic rubber during storage. Table IIIB shows that the zinc oxide-stabilized oil-extended synthetic rubber produces vulcanized rubber compositions fully equivalent in properties to the unstabilized rubber (in this test all rubbers were compounded before ageing).

Other high-aromatic oils found to be equivalent to the Shell SPX-97 utilized in the above Examples are Sundex 53 and Dutrex 20. Additional oils suitable for extending hydrocarbon rubbery butadiene polymers are disclosed in Specification No. 737,086, especially in Table 1 thereof. The amount of oil employed in extending the rubber generally runs from 20 to 100 phr, although 30 to 60 phr of oil is more usual. The rubbery polymers comprise at least 50% of a conjugated butadiene-1,3 hydrocarbon polymerized therein.

The Examples show that a relatively small proportion of the finely-divided inorganic pigment effectively stabilizes the oil-extended synthetic rubber. The range of the pigment employed is from about 0.5 to 3.0 phr, although appreciable stabilization results from the addition of as little as 0.1 phr of the pigment.

In addition to the technique of admixing the finely-divided inorganic pigment with a synthetic rubber latex, as illustrated above, the pigment can be admixed with the freshly produced oil-extended rubber in other manners. An aqueous dispersion of the pigment can be admixed with an aqueous dispersion of the oil-extended rubber and the mixture can then be coagulated. The pigment can be mixed with either the synthetic rubber latex or the oil dispersion prior to mixing said latex and dispersion together. Alternatively, the finely-divided pigment, either as such or mixed with a non-aqueous solvent or other liquid, can be mixed with a non-aqueous solution or dispersion of the synthetic rubber, the extending oil or the oil-extended synthetic rubber. In addition, the pigment can be mechanically mixed or milled into the solid synthetic rubber, as on a rubber mill or in an internal rubber mixer, the rubber being either in the extended or unextended form; in the latter case the pigmented unextended synthetic rubber is then oil-extended by suitable admixture with an oil.

#### WHAT WE CLAIM IS:—

1. An unvulcanized oil-refined rubbery polymer of a conjugated diolefin having up to 8 carbon atoms stabilized against rapid loss

of its initial Mooney plasticity value upon ageing prior to vulcanization, said rubber comprising 0.1 to 3 parts per hundred of rubber of a finely-divided inorganic rubber pigment admixed therewith, said pigment being selected from zinc oxide, magnesium oxide, calcium silicate and silicon dioxide.

2. A rubber according to claim 1, in which the rubber comprises butadiene - styrene copolymer.

3. A method of stabilizing an oil-extended rubbery polymer or copolymer of a conjugated diolefin having up to 8 carbon atoms comprising admixing a relatively small proportion of a finely-divided inorganic rubber pigment selected from zinc oxide, magnesium oxide, calcium silicate and silicon dioxide with the unaged oil-extended rubber prior to the usual compounding of the rubber for vulcanization, whereby the Mooney plasticity of the unvulcanized oil-extended rubber is stabilized.

4. A method according to claim 3, in which the rubber comprises a butadiene-styrene copolymer.

5. A method according to claim 3 or 4, in which an aqueous dispersion of the pigment is admixed with an aqueous dispersion of said oil-extended rubber and the mixture is then coagulated.

6. A method according to claim 3 or 4, in which the rubber pigment is admixed with a non-aqueous solvent dispersion of the rubber, the extending oil or the said oil-extended rubber.

7. A method according to claim 4, in which the rubber pigment is mechanically admixed with solid polymer.

8. A stabilized unvulcanized oil-extended synthetic rubber substantially as hereinbefore described with reference to the Examples.

9. A method of stabilizing an oil-extended synthetic rubber substantially as hereinbefore described with reference to the Examples.

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